

Diels–Alder Reactions of Alumina- and Magnesacyclopentadienes

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Abstract— $[4\pi+2\pi]$ -Cycloaddition of substituted alumina- and magnesacyclopenta-2,4-dienes with such dienophiles as maleic anhydride, *N*-methylmaleimide, 1,4-benzoquinone, and 1,4-naphthoquinone resulted in the formation of the corresponding fused alumina- and magnesanorbornenes whose hydrolysis gave isobenzofuran, isoindole, naphthalene, and anthracene derivatives in high yields.

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Diels–Alder reactions of organic 1,3-dienes and dienophiles, including those containing heteroatoms, underlie one of the most popular and extensively used methods for the synthesis of difficultly accessible unsaturated carbo- and heterocyclic compounds with various structures [1–3]. Development of preparative procedures for the synthesis of metallacyclopentadienes [4–6] made it possible to involve some of them [7, 8] in $[4+2]$ -cycloadditions with dienophiles. Prior to our studies, no data have been reported on Diels–Alder reactions with alumina- or magnesacyclopenta-2,4-dienes.

We examined reactions of various dienophiles with 1-ethyl(chloro)aluminacyclopenta-2,4-dienes generated from internal alkynes and RAlCl_2 ($\text{R} = \text{Et}, \text{Cl}$) in the presence of Cp_2ZrCl_2 as catalyst [9]. As dienophiles we used maleic anhydride, *N*-methylmaleimide, 1,4-benzoquinone, and naphthoquinone [10]. While developing optimal conditions for the $[4+2]$ -cycloaddition of aluminacyclopenta-2,2-dienes to the above dienophiles we found that the initial aluminum compounds (RAlCl_2 , $\text{R} = \text{Et}, \text{Cl}$) effectively catalyze the cycloaddition process; therefore, all experiments were carried out using excess RAlCl_2 .

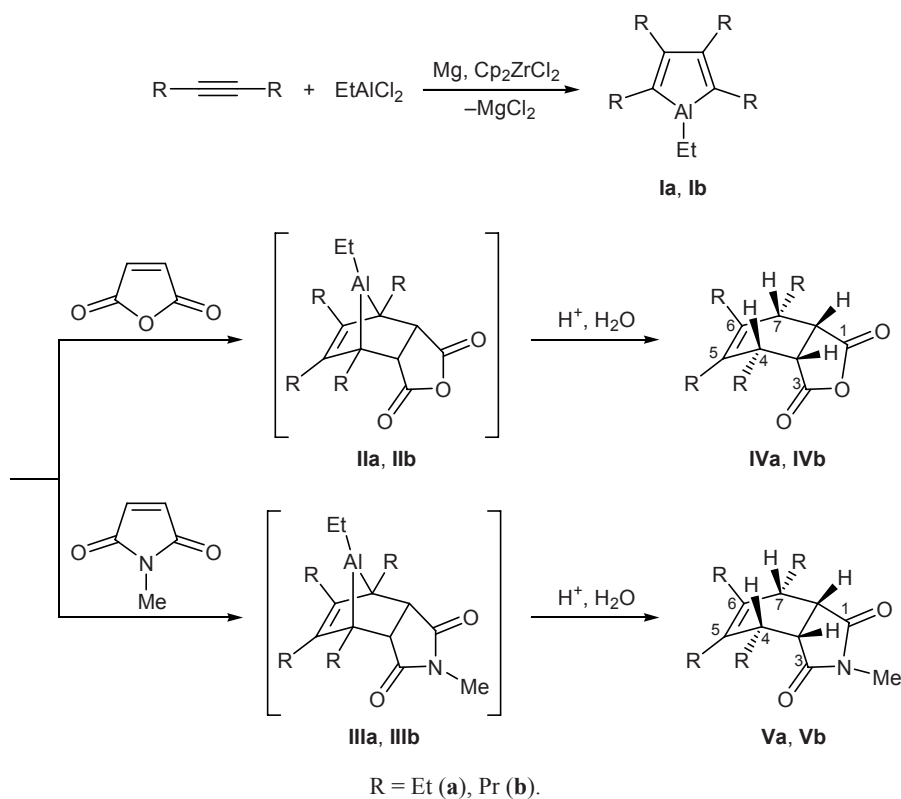
1,2,3,4,5-Pentaethylaluminacyclopenta-2,4-diene (**Ia**) reacted with maleic anhydride in 6 h at room temperature ($\sim 20^\circ\text{C}$) to produce adduct **IIa**; after hydrolysis of the reaction mixture with 8–10% hydrochloric acid we isolated $\sim 85\%$ of 4,5,6,7-tetraethyl-3a,4,7,7a-tetrahydro-2-benzofuran-1,3-dione (**IVa**) (Scheme 1). The IR spectrum of **IVa** contained a strong absorption

band at 1760 cm^{-1} , which is typical of anhydride carbonyl groups. In the ^{13}C NMR spectrum of **IVa** we observed signals from carbon atoms in the ethyl groups and signals at δ_{C} 138.03, 42.51, and 40.76 ppm, which were assigned to carbon atoms in the cyclohexene ring. The carbonyl carbon nuclei resonated at δ_{C} 172.20 ppm. The ^{13}C NMR spectrum contained eight signals, indicating a high symmetry of the molecule. This is possible only when the ethyl groups on C^4 and C^7 are oriented *cis* with respect to each other (the cyclohexene ring adopts a *boat* conformation). The 4-H and 7-H protons gave rise to a narrow multiplet centered at δ 3.27 ppm in the ^1H NMR spectrum (halfwidth $w_{1/2} = 8\text{ Hz}$); this suggests a small coupling constant between *cis*-oriented protons on C^{3a} and C^{7a} . Thus the five-membered furan ring is oriented *cis* with respect to the ethyl groups on C^4 and C^7 . The above findings confirm the structure of **IVa** as 4,5,6,7-tetraethyl-3a,4,7,7a-tetrahydro-2-benzofuran-1,3-dione.

Aluminacyclopentadienes **Ia** and **Ib** generated by catalytic cycloaluminumation of hex-3-yne and oct-4-yne with EtAlCl_2 [9] reacted with maleic anhydride and *N*-methylmaleimide to give aluminanorbornene derivatives **IIa**, **IIb**, **IIIa**, and **IIIb**. The latter were subjected to hydrolysis with 8–10% hydrochloric acid to obtain isobenzofuran and isoindole derivatives **IVa**, **IVb**, **Va**, and **Vb** in 70–85% yield (Scheme 1).

1,4-Benzoquinone and 1,4-naphthoquinone showed a low reactivity as dienophiles toward 1-ethylaluminacyclopenta-2,4-dienes **Ia** and **Ib**. On the other hand, they fairly readily reacted with 1-chloroaluminacyclo-

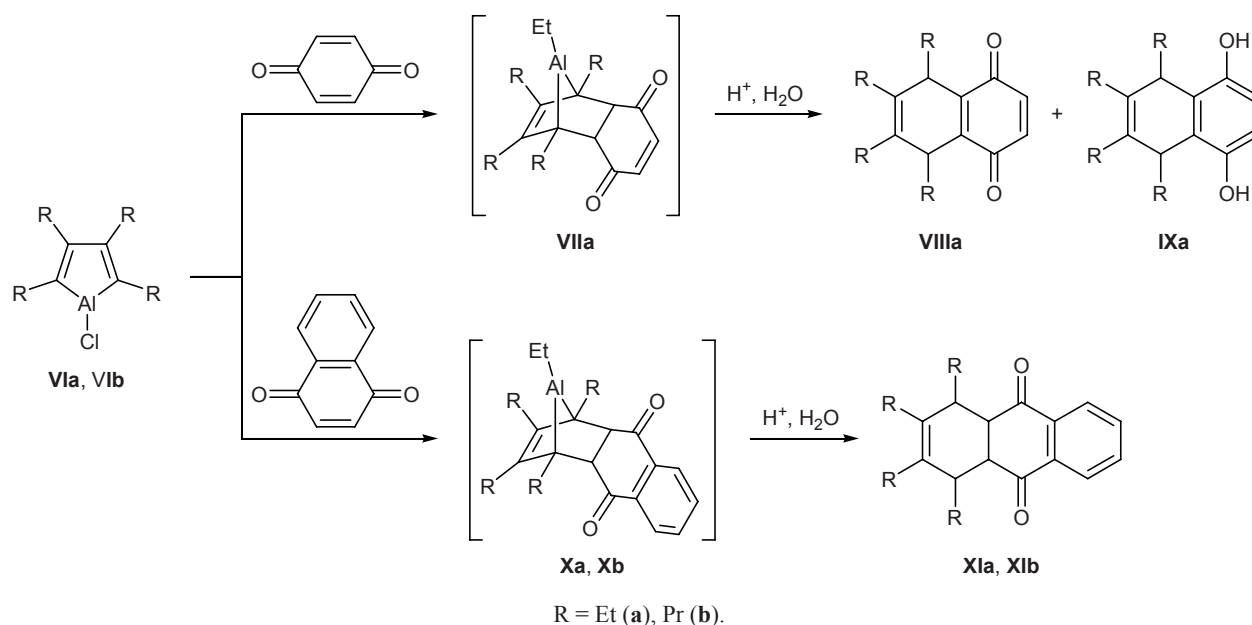
Scheme 1.



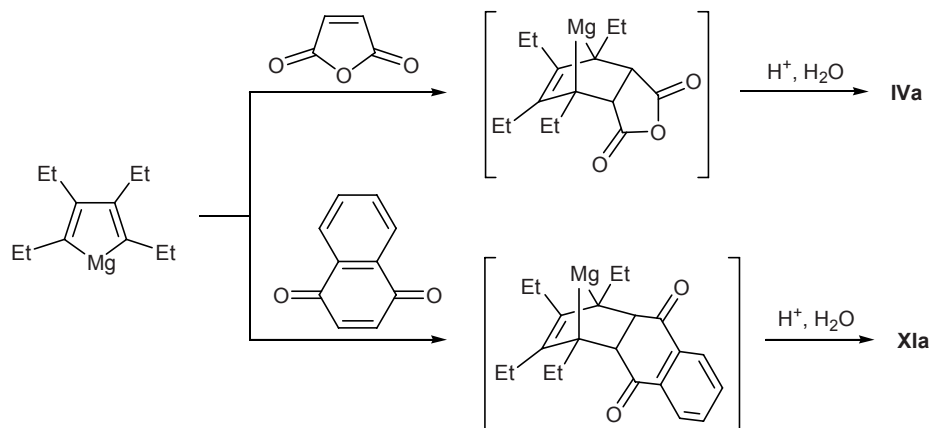
penta-2,4-dienes **VIa** and **VIb** generated *in situ* by cycloalumination of the corresponding internal alkynes with AlCl_3 , the ratio dienophile–compound **VI** being 2:1 (Scheme 2). The reaction of 1-chloro-2,3,4,5-tetraethylaluminacyclopenta-2,4-diene (**VIa**) with 1,4-ben-

zoquinone in THF at $\sim 20^\circ\text{C}$ (5 h), followed by hydrolysis, gave an approximately equimolar mixture of compounds **VIIIa** and **IXa** with an overall yield of $\sim 75\%$. Presumably, compounds **VIIIa** and **IXa** were formed via successive dehydrogenation of the hydroly-

Scheme 2.



Scheme 3.



ysis product of adduct **VIIa** by the action of excess 1,4-benzoquinone [10, 11] in acid medium [12–14]. By cycloaddition of 1-chloroaluminacyclopenta-2,4-diene (**VIa**) to 1,4-naphthoquinone (THF, $\sim 20^\circ\text{C}$, 6 h) and subsequent hydrolysis of the reaction mixture we obtained tetrahydroanthraquinone **XIa** in $\sim 70\%$ yield (Scheme 2).

The structure of compound **XIa** was determined on the basis of two-dimensional ^1H – ^1H COSY and HSQC experiments. The ^{13}C NMR spectrum of **XIa** contained 11 signals, indicating that molecule **XIa** possesses a symmetry plane. Signals from the carbonyl carbon atoms and carbon atoms at the double bond ($\text{C}^2=\text{C}^3$) appeared in a weak field. The carbon nuclei resonating in a strong field (at δ_{C} 38.89 ppm) showed coupling with CH proton resonating at δ 3.49 ppm; therefore, the signal at δ_{C} 38.89 ppm was assigned to the C^1 and C^4 atoms. Diastereotopic methylene protons in the ethyl groups on C^1 and C^4 gave two multiplets. Analogous diastereotopic splitting was observed for the allylic methylene protons at C^2 and C^3 .

We also tried to involve 2,3,4,5-tetrasubstituted magnesacyclopenta-2,4-dienes [15] in [4+2]-cycloaddition reactions with some dienophiles. However, unlike aluminacyclopenta-2,4-dienes, magnesacyclopentadienes generated *in situ* failed to react under analogous conditions. Taking into account the data of [16, 17], we presumed that diethyl ether used as solvent in the cyclomagnesation of acetylenes deactivated magnesacyclopentadienes via coordination at the magnesium atom. In fact, after removal of diethyl ether from the reaction mixture by evacuation and subsequent washing of the residue with two portions of benzene we succeeded in obtaining Diels–Alder adducts of 2,3,4,5-tetraethylmagnesiancyclopenta-2,4-di-

ene with maleic anhydride and 1,4-naphthoquinone (benzene, 80°C , 12 h). Hydrolysis of the reaction mixture gave compounds **IVa**, and **XIa**, respectively, in $\sim 40\%$ yield (Scheme 3).

The yield of adducts **IVa** and **XIa** can be improved by carrying out the reactions of magnesacyclopentadiene with the corresponding dienophiles in the presence of a catalytic amount (10 mol %) of AlCl_3 or $\text{BF}_3 \cdot \text{Et}_2\text{O}$ [16, 17]. The use of the above Lewis acids allowed us to shorten the reaction time to 8 h, reduce the temperature to ambient, and raise the yield of **IVa** and **XIa** to 60%. The reaction of tetraethylmagnesiancyclopentadiene with *N*-methylmaleimide even in the presence of AlCl_3 or $\text{BF}_3 \cdot \text{Et}_2\text{O}$ on heating in boiling toluene (24 h) gave no more than 8% of adduct **Va**.

EXPERIMENTAL

The IR spectra were recorded from films on a Specord 75IR spectrometer. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1306 spectrometer (ion source temperature 200°C). The ^1H and ^{13}C NMR spectra were measured from solutions in CDCl_3 on a JEOL FX-90Q spectrometer at 89.55 (^1H) and 22.5 MHz (^{13}C); the two-dimensional spectra (^1H – ^1H COSY and HSQC) were obtained on a Bruker Avance 400 instrument (400.13 MHz for ^1H and 100.62 MHz for ^{13}C). The reaction mixtures were analyzed by GLC on a Chrom-5 chromatograph (1200 \times 3-mm column packed with 5% of SE-30 or 15% of PEG-6000 on Chromaton N-AW; carrier gas helium). All reactions with organometallic compounds were carried out in a stream of dry argon. Tetrahydrofuran and diethyl ether were dried by boiling over metallic sodium. Commercially available EtAlCl_2 (86%) and AlCl_3 were used. The yields of organoalu-

minum compounds were determined by GLC analysis of the hydrolysis products using *n*-hexadecane as internal standard.

Reactions of 1-ethyl-2,3,4,5-tetraalkylalumina-cyclopenta-2,4-dienes with dienophiles (general procedure). A glass reactor was filled with argon and charged at $\sim 0^\circ\text{C}$ under stirring with 1.0 mmol of Cp_2ZrCl_2 , 7.5 mmol of magnesium powder, 10 mmol of hex-3-yne or oct-4-yne, 10 ml of THF, and 7.5 mmol of EtAlCl_2 or AlCl_3 . The mixture was allowed to warm up to room temperature ($20\text{--}22^\circ\text{C}$) and stirred for 8 h, 14 mmol of the corresponding dienophile was added, and the mixture was stirred until the reaction was complete, treated with 10% hydrochloric acid, and extracted with diethyl ether or hexane. The extract was dried over MgSO_4 , volatile compounds were removed under reduced pressure, and the residue was passed through a thin layer of neutral aluminum oxide and analyzed.

Reactions of 2,3,4,5-tetraethylmagnesiumcyclopenta-2,4-diene with dienophiles (general procedure). A glass reactor was filled with argon and charged at $\sim 0^\circ\text{C}$ under stirring with 1.0 mmol of Cp_2ZrCl_2 , 10 mmol of hex-3-yne, and 15 mmol of BuMgHlg ($\text{Hlg} = \text{Cl}, \text{Br}$) as a 2 M solution in diethyl ether. The mixture was allowed to warm up to room temperature ($20\text{--}22^\circ\text{C}$), stirred for 2 h, and evacuated, the residue was washed with two portions of benzene, 15 mmol of the corresponding dienophile was added, and the mixture was stirred until the reaction was complete, treated with 10% hydrochloric acid, and extracted with diethyl ether or hexane. The extract was dried over MgSO_4 , volatile compounds were removed under reduced pressure, and the residue was passed through a thin layer of neutral aluminum oxide and analyzed.

4,5,6,7-Tetraethyl-3a,4,7,7a-tetrahydro-2-benzofuran-1,3-dione (IVa). Yield 85%, R_f 0.42 (hexane–diethyl ether, 2:1). IR spectrum, ν , cm^{-1} : 3350, 2920, 1760, 1390, 1150, 1070, 1020, 980, 920. ^1H NMR spectrum, δ , ppm: 0.84 t (6H, CH_3 , $J = 7.0$ Hz), 1.03 t (6H, CH_3 , $J = 7.0$ Hz), 1.83–2.08 m (4H, CH_2), 2.01 m (2H, CH), 2.03 q (4H, CH_2 , $J = 7.0$ Hz), 3.27 m (2H, CH, $w_{1/2} = 8$ Hz). ^{13}C NMR spectrum, δ_C , ppm: 12.27, 14.67, 19.64, 20.41, 40.76, 42.51, 138.03, 172.20. Found, %: C 72.48; H 8.96. M 264. $\text{C}_{16}\text{H}_{24}\text{O}_3$. Calculated, %: C 72.69; H 9.15.

4,5,6,7-Tetrapropyl-3a,4,7,7a-tetrahydro-2-benzofuran-1,3-dione (IVb). Yield 72%, R_f 0.44 (hexane–diethyl ether, 2:1). ^1H NMR spectrum, δ , ppm: 0.84 t (6H, CH_3 , $J = 7.0$ Hz), 1.03 t (6H, CH_3 , $J = 7.0$ Hz),

1.78–2.10 m (18H, CH, CH_2), 3.23–3.34 (2H, CH). ^{13}C NMR spectrum, δ_C , ppm: 13.50, 13.96, 20.74, 22.10, 29.82, 31.03, 39.54, 42.91, 137.82, 172.11.

4,5,6,7-Tetraethyl-2-methyl-2,3,3a,4,7,7a-hexahydro-1H-isoindole-1,3-dione (Va). Yield 85%, R_f 0.38 (hexane–diethyl ether, 2:1). IR spectrum, ν , cm^{-1} : 3350, 2950, 2880, 1760, 1690, 1430, 1370, 1280, 1160, 1060, 1020, 980, 920. ^1H NMR spectrum, δ , ppm: 0.78 t (6H, CH_3 , $J = 7.0$ Hz), 1.05 t (6H, CH_3 , $J = 7.0$ Hz), 1.48–2.20 m (10H, CH, CH_2), 2.92 s (3H, CH_3N), 3.00–3.11 m (2H, CH). ^{13}C NMR spectrum, δ_C , ppm: 12.27, 14.29, 19.92, 23.31, 24.97, 40.96, 41.35, 136.88, 178.07. Found, %: C 73.49; H 9.64; N 4.97. $\text{C}_{17}\text{H}_{27}\text{NO}_2$. Calculated, %: C 73.60; H 9.81; N 5.05.

2-Methyl-4,5,6,7-tetrapropyl-2,3,3a,4,7,7a-hexahydro-1H-isoindole-1,3-dione (Vb). Yield 72%, R_f 0.37 (hexane–diethyl ether, 2:1). ^1H NMR spectrum, δ_C , ppm: 0.78 t (6H, CH_3 , $J = 7.0$ Hz), 1.02 t (6H, CH_3 , $J = 7.0$ Hz), 1.35–2.22 m (26H, CH, CH_2), 2.90 s (3H, CH_3N), 3.02–3.15 m (2H, CH). ^{13}C NMR spectrum, δ_C , ppm: 13.59, 14.68, 22.92, 23.31, 24.97, 33.91, 40.96, 41.35, 136.88, 180.17.

5,6,7,8-Tetraethyl-1,4,5,8-tetrahydronaphthalene-1,4-dione (VIIIa). Yield 25%, R_f 0.31 (hexane–diethyl ether, 2:1). ^1H NMR spectrum, δ , ppm: 0.82–1.09 m (12H, CH_3), 1.17–2.59 m (8H, CH_2), 3.45 m (2H, CH), 5.92 m (2H, $\text{CH}=\text{CH}$). ^{13}C NMR spectrum, δ_C , ppm: 13.84, 14.03, 24.99, 29.57, 39.85, 134.50, 136.19; 145.34, 187.22. Found, %: C 78.67; H 8.73. M 272. $\text{C}_{18}\text{H}_{26}\text{O}_2$. Calculated, %: C 78.79; H 9.55.

5,6,7,8-Tetraethyl-5,8-dihydronaphthalene-1,4-diol (IXa). Yield 24%, R_f 0.39 (hexane–diethyl ether, 2:1). ^1H NMR spectrum, δ , ppm: 0.84–1.07 m (12H, CH_3), 1.17–2.59 m (8H, CH_2), 3.35–3.68 m (2H, CH), 6.23–6.71 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C , ppm: 13.01, 13.57, 19.88, 25.33, 39.43, 116.07, 130.50, 136.06, 146.71. M 274.

1,2,3,4-Tetraethyl-1,4,4a,9,10,10a-hexahydroanthracene-9,10-dione (XIa). Yield 70%, R_f 0.67 (hexane–diethyl ether, 2:1). IR spectrum, ν , cm^{-1} : 3400, 2950, 1760, 1710, 1650, 1590, 1280, 1160, 1020, 980, 920. ^1H NMR spectrum, δ , ppm: 0.87 t (6H, CH_3 , $J = 7.0$ Hz), 0.94 t (6H, CH_3 , $J = 7.0$ Hz), 1.47–1.66 m (4H, CH_2), 1.96–2.29 m (4H, CH_2), 2.12 m (2H, CH), 3.49 m (2H, CH), 7.80–8.15 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C , ppm: 13.54, 13.74, 20.28, 23.98, 38.89, 126.20 (C_{arom}), 132.30 (C_{arom}), 133.91 (C_{arom}), 134.66, 147.94, 184.62.

1,2,3,4-Tetrapropyl-1,4,4a,9,10,10a-hexahydro-anthracene-9,10-dione (XIb). Yield 58%, R_f 0.66 (hexane–diethyl ether, 2:1). ^1H NMR spectrum, δ , ppm: 0.88 t (6H, CH_3 , $J = 7.0$ Hz), 0.98 t (6H, CH_3 , $J = 7.0$ Hz), 1.47–1.68 m (8H, CH_2), 1.98–2.24 m (8H, CH_2), 3.49 m (2H, CH), 7.76–8.05 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C , ppm: 13.89, 14.24, 20.48, 24.98, 30.87, 32.51, 33.88, 39.52, 126.17 (C_{arom}), 133.66 (C_{arom}), 134.28 (C_{arom}), 147.35, 184.21.

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